Investigation of Small Amounts of Water
in Lithium Greases by Infrared Absorbtion

By

JAMES EDWARD EDMUNDSON
LIEUTENANT, UNITED STATES NAVY

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INVESTIGATION OF SMALL AMOUNTS OF WATER
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By

James Edward Edmundson

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TABLE OF CONTENTS

INDEX OF FIGURES

INDEX OF FIGURES

CHAPTER I

INTRODUCTION

Discussion of Lubricating Greases

For many years grease making was considered an art,
but within the last two decades this art has been subjected
to a rather thorough scientific investigation.

Greases are essentially a thickened oil with particles
of thickening agent, usually soaps, highly dispersed in the
oil. It is convenient to think of a lubricating grease as
a honeycomb of soap filled with oil.

Generally, grease preparation consists of mixing the
soap and oil, and heating to produce a well dispersed mix-
ture. The heating also tends to reduce the water content.
The dispersed mixture is then cooled to a prescribed temp-
erature and may be milled to improve homogeneity and to
obtain desired fiber length.

Most greases consist of soap, mineral oil, and addi-
tives. The soaps usually have a saturated fatty acid com-
ponent of 16 - 18 carbon atoms and a metallic component of
Ca, Na, Li, or Al. Sometimes binary mixtures of metallic
soaps are used.[1] Lubricating greases are often classified
by these metallic components.

Mineral oils in greases are generally paraffinic or
naphthenic oils of a non-polar nature consisting of cyclic

or aromatic rings with extensive side chains.[13] In
silicone greases, the mineral oil is replaced by silicone.
Additives are employed to improve some property of the
grease. Some examples are rust preventitives, oxidation
inhibitors, extreme pressure agents, and water resistance
agents.[6] A small amount of water is almost always present,
depending on the type of grease. This water content is
usually less than one percent by weight. A very small
amount of excess alkali or fatty acid is normally present.

The structure of lubricating greases has been investi-
gated largely by use of X-ray diffraction and electron micro-
scope methods. These have shown that the soap and oil con-
stitute two separate phases. The oil is more or less soap
free and is held in the soap by capillary forces. It is
suspected that small amounts of soap remain highly dispersed
throughout the oil.[2,6,10] The soap appears in the form
of fibers which aggregate into larger fibers and into clus-
ters. The soap particles are often oriented, as in Li
greases, but may not be, as in Al greases.[5] The fibers
vary in size a good deal, but are on the order of .1 micron
wide and 1 to 50 microns long.[2,5] Fiber configurations
may resemble rods, elongated ribbons, or twisted fibrils.
The size and shape are dependent on the oil used in the
grease, the rate of cooling and the gelling temperature
employed during manufacture. For example, Li stearate forms

fine fibers in naphthenic oil and coarse fibers in paraffinic oil.[8]

Almost all lubricating greases contain some water. Water and other polar compounds can coordinate with the metal atoms and break down the fiber structure. On the other hand, in Ca greases, water stabilizes the soap structure and the grease will break down and separate when dehydrated. Some of the water present is known to be highly dispersed in the oil phase, and it is believed that some of the water is hydrated or coordinated with the metal components of the soap. Very little information is available regarding the manner in which water appears in lubricating greases.

Several excellent micrographs of various greases are presented in reference 2.

Many properties of greases depend upon the grease composition and the size and configuration of the soap particles. The absolute dimensions, the length-diameter ratio, and the state of aggregation of the soap fibers can all be associated with certain grease properties. For instance, mechanical breakdown is directly connected to the reduction in length of soap fibers, and consistency is known to be influenced by the length-diameter ratio. Length-diameter ratios are of the order of 10:1 to 200:1.

Among the many factors presently being considered in

the development of greases is the influence of the presence of water. Determination of the amount of water present in the grease is logically an important item in such investigation and development, and it is also important during certain manufacturing processes, such as dehydration. Therefore, it is necessary to have a satisfactory method for determination of water in lubricating greases.

Methods of Water Determination in Lubricating Greases

The best laboratory method for water determination appears to be a modified Karl Fischer titration. The analytical procedure usually involves an azeotropic distillation followed by a Karl Fischer titration using a microburet. This increases sensitivity to about .01% by weight, and has been applied successfully to many types of lubricating greases.[15,16,17] A.S.T.M. Method D128, an azeotropic distillation, is not sufficiently sensitive to use when the grease sample contains less than .25% water. Use of the Karl Fischer micro method yields better precision and permits close control of dehydration during manufacture.

Additional methods of water analysis which could be applied to lubricating greases include: infrared adsorbtion;[19] use of methylene blue;[20] electrical methods;[21,22] use of heavy water;[23] dielectric constants; and infrared absorbtion.

The use of infrared absorbtion for analytical purposes

is not new.[24] It is regularly employed in industry in
analyzing for one component in both batch and continuous
processes, and many laboratories make frequent use of it.[29]
However, apparently no one has applied infrared absorbtion
to the analysis of water in lubricating greases. Actually,
it is well suited for such a use. Analyses can be quickly
and accurately performed, samples can be prepared without
complication, and operators can be trained easily. To those
investigating the structure of lubricating greases, infrared
absorbtion methods offer another advantage in that the
grease is not altered during sample preparation or analysis.

Outline of Work

A double beam infrared spectrophotometer was used for
differential analysis of several lubricating grease and
mineral oil samples of known water content. The analysis
data were plotted in accordance with accepted procedures
and appear to conform with Beer's Law.

Numerous tests were performed to determine suitable
methods of sample preparation, cell thickness and instrument
operation. Spectra of some of the grease components were
prepared, and visually compared with the grease spectrum.

Comparison, or difference, spectra of the grease samples
were prepared using samples ranging from .02% to 1.20% water
content by weight. Usable data were averaged and plotted

according to standard procedures.

Known amounts of water were added to samples of the same mineral oil that was used in the manufacture of the grease, and difference spectra of these water in oil samples were prepared. The samples were agitated by an ultrasonic generator and difference spectra were recorded. After the agitated samples had stood overnight, their difference spectra were obtained again, and all data were averaged and plotted.

The results of the analyses were critically examined to determine if they represented a useful analytical method, and to see if they contained information pertaining to the manner in which water is held in lubricating grease.

CHAPTER II

EXPERIMENTAL PROCEDURE

Description of Apparatus

A Perkin-Elmer Model 21 infrared spectrophotometer was employed for the preparation of differential spectra. The instrument was checked by performing operating tests as prescribed in reference (30), and it was found to be operating properly. In addition, the instrument was inspected, tested, and adjusted by a Perkin-Elmer representative who reported it to be in excellent working order.

Certain errors are inherent in the use of this instrument. They can be classified as random errors and systematic errors. Some random errors are caused by small fluctuations of intensity and can be attributed to the servo system, the amplifier, and the frictional forces in the recorder system. The effect of the recorded position of a band peak is also considered a random error. The primary systematic errors are concerned with finite slit width, optical attenuation, stray or scattered light, and the 0% and 100% lines.[25,26,27,28] These errors and their sources were studied and measures were taken to minimize them in this analysis.

In order to avoid inserting errors into the analysis, it is essential that the instrument be set up in precisely the

same manner for every recording. Therefore, the most useful data will be generated when the same instrument settings and cell thicknesses are used for every run. It is important to remember that in most cases extinction coefficients are not interchangeable. This means that all data must be collected from the same instrument, and that exact agreement is not to be expected between data from different instruments.[25,26]

Operating Procedure

The differential analysis method consists of placing a reference sample in one infrared beam and the sample to be tested in the other beam. The spectrophotometer compares the energy transmitted by each sample cell and records the difference spectrum. This procedure tends to compensate for some of the systematic and random errors. To further reduce random errors, the water band region was scanned at a small fixed slit width, the auto suppressor was generously used, the drift, 0% and maximum transmission settings were checked before each run, and the results of several recordings at a given concentration were averaged. A true 100% line can be obtained when using difference spectra, but it was not possible in this case because of the great difficulty encountered in obtaining reproducible cell thicknesses. Calculation of empirical corrections for optical attenuation and finite slit width errors were not attempted. These corrections did not

appear to be justified since they would be very small under the conditions of this experiment, and the cell thickness error would nullify their value anyway. Stray and scattered light errors were essentially eliminated by use of the differential method, short wave lengths and a small slit width.

The infrared spectrophotometer should be maintained and operated in a constant humidity room. Since the instrument used was not in such a room, and the analysis was for small amounts of water, the effect of humidity was checked. A non-permeable hood was constructed which enclosed the open air path of the infrared beams, but allowed insertion of the two test cells into their holders on the instrument. Two windows of Saran Wrap were provided to allow free passage of the beams through the hood. Several dishes of anhydrous magnesium perchlorate were placed inside, and the hood was sealed to the body of the instrument with masking tape. It was hoped that this dessicant would dry out the air path inside the source side of the instrument, as well as the open air path. The system was allowed to stand for about eighteen hours, and then difference spectra of some grease samples were obtained. The hood was removed and the area was well ventilated for over thirty minutes. The hood was then replaced and the same difference spectra were run off. Comparison of the two sets of spectra indicated that the humidity difference had no discernable effect. It was

concluded that if there was an error caused by day to day humidity variations, it was too small to be concerned with at this time.

Of the several water bands available, the one in the neighborhood of 3 microns gave the best results. This region, 2 to 6 microns, was scanned at a speed setting of 5 (about 1 micron per minute), with a constant slit width of 25 microns. The slit width was set manually from the low side with no overshoot to minimize error. Prior to each run the amplifier drift was checked and adjusted, as were the 0% and maximum transmission settings. The best response curve was obtained for a Gain setting of 5 and Response setting of 1, so these settings were used. The Auto Suppressor was set rather high, at a setting of 6, in the hope of reducing random errors. The intensity setting was .3 amps.

Because variations in cell thickness made it impossible to obtain a good base line by comparing identical samples, several methods of interpreting the difference spectra were tried. The most satisfactory method involved drawing a base line between selected peaks of the recorded trace. I_o was measured from the 0% line to this base line and I was measured from the 0% line to the water band peak at 3.05 microns. Several $\log I_o/I$ values were computed and averaged for each concentration tested. Plots of $\log I_o/I$ vs gms. of water per 100 gms. of sample grease were prepared from these averaged values. See figure 1.

FIGURE 1

Cell Thickness = .12 mm
Water Content = .80%

I_o = 79.5
I = 35.

Log $\frac{I_o}{I}$ = .356
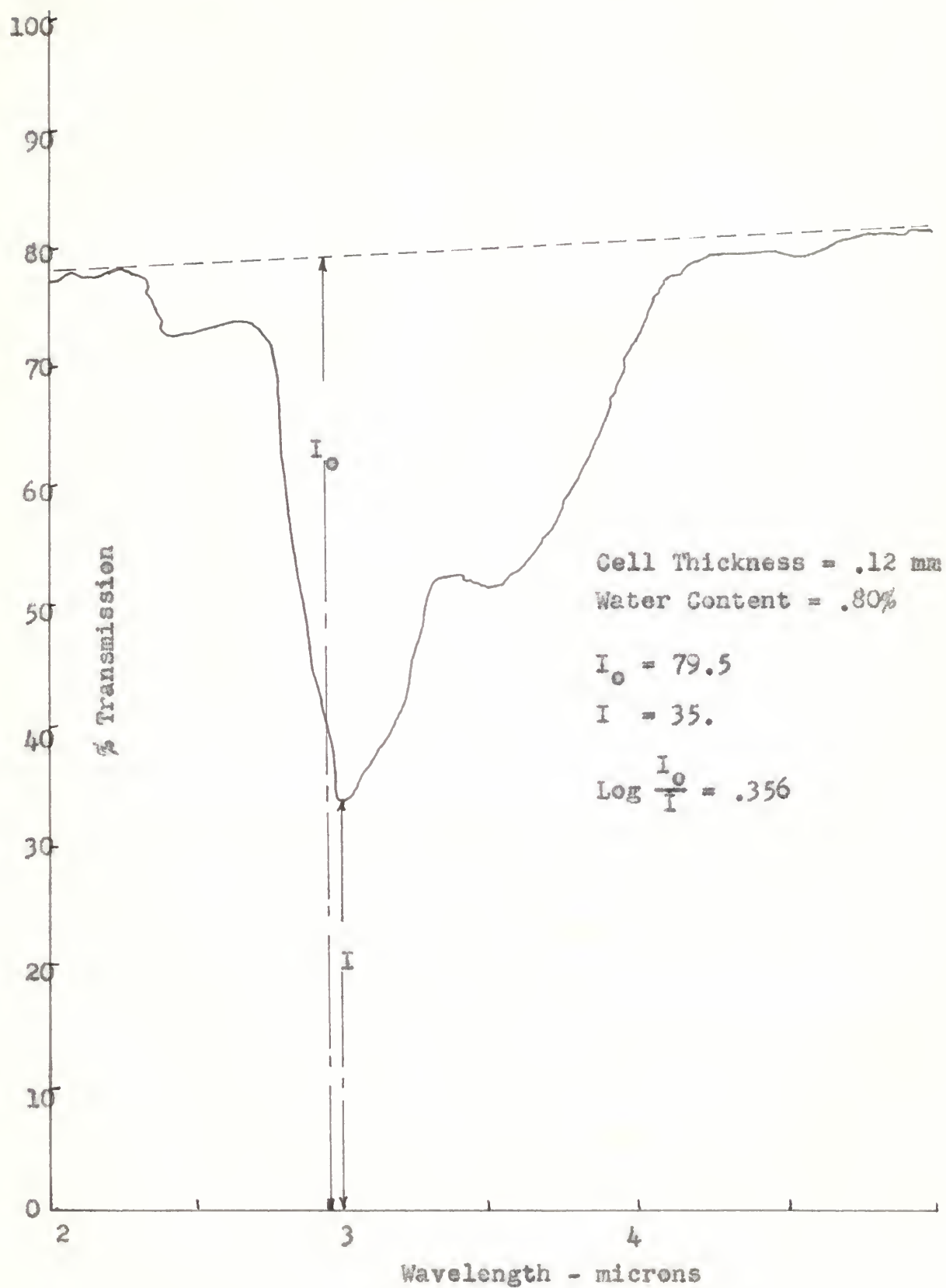
Grease Samples

Eight samples of a Li grease and the following water determination data were supplied by the SOCONY MOBIL OIL COMPANY, INC.

GREASE SAMPLE NO.	% WATER BY WEIGHT	
	KARL FISCHER	XYLOL
59520	.49 %	.6 %
59521	.40 %	.6 %
59522	.08 %	--
59523	.02 %	--
59524	1.24 %	.9 %
59525	1.14 %	.7 %
59526	.12 %	--
59527	.02 %	--

Sodium chloride salt crystals were selected for the cell windows because of their cheapness and excellent range of infrared transmission. The crystals measured one inch in diameter and one quarter inch thick.

An effort to prepare samples for analysis by the "notch" method was not successful. This consisted of cutting a small notch or shallow groove in a plastic ruler and drawing it over the surface of a grease covered salt crystal. The grease

proved to be too cohesive and spectrum reproducibility was almost impossible, so this method was abandoned.

The "sandwich" method was used for all data collecting runs. Samples were prepared in this method by sandwiching two thin spacers and a layer of grease between two salt crystals. The crystals were carefully pressed together until the grease ceased to leak out at the edges, and all large bubbles had escaped. After a little practise, a reasonable reproducibility was achieved. This method is by no means exact enough for a precise analysis as indicated by the fact that a satisfactory base line could not be obtained when identical greases were compared. Nevertheless, it was the best thing available at the time and proved satisfactory for general purposes. This appears to be the largest error involved in this analysis. The quarter moon-shaped spacers were cut from brass shim material and hard surfaced cardboard. After experimenting with different cell thicknesses, two cells were selected. One employed .12mm shim material and the other .68mm cardboard as spacers. Measurements were made by micrometer. It is realized that the samples within the cells were actually somewhat thicker than the spacer measurements indicate, but the same spacers were used in each cell for all runs.

The lubricating grease spectrum has a large C-H band peak in the region of 3.5 microns. It was expected that

this might cause some interference with the water band at 3 microns,[29] but no apparent difficulty was observed.

The grease samples appeared to have been taken from at least two different batches, so the spectra of several samples were visually compared. All the spectra examined were practically coincident in the water band region, so it seemed justifiable to take difference spectra of greases from two different batches as long as they were the same type of grease.

The grease placed in the reference beams was always of lower water content than the one placed in the sample beam. This kept all the deflections, or peaks, headed in the same direction. The reference grease cell was normally left in the instrument and all greases of higher water content were compared with it. This procedure was gleefully repeated many times.

The possibility of the reference grease spectrum actually changing during a long period in the instrument was investigated. Continuously cycled runs for about forty-five minutes produced no significant change in the normal or the difference spectra of the reference grease. Any change was apparently too small to be detected.

Grease Components

The following components of the test grease were

supplied by SOCONY MOBIL OIL COMPANY, INC.

	SAMPLE NO.
Mineral Oil	59534
Fatty Acid	59535
$LiOH.H_2O$	59536
Slaked Lime Flour	59537

Spectra were prepared for each of the components except the
slaked lime flour. These spectra were visually compared
with the grease spectrum to determine, if possible, their
contribution to the grease spectrum.

Oil Samples

Enough mineral oil was available to make up water in
oil samples in the same concentration range as the grease
samples. The following samples were prepared by adding known
amounts of distilled water to measured amounts of oil. The
samples were shaken vigorously several times and allowed to
stand overnight before their difference spectra were obtained,
using the anhydrous oil as the reference. The same procedure
was employed in obtaining these spectra as was used for the
grease samples.

SAMPLE NO.	% WATER BY WEIGHT
1	.29 %
2	.37 %
3	.44 %
4	.49 %
5	.55 %
6	.59 %
7	.74 %
8	.89 %

After the comparison runs were made, the oil samples were placed in a General Electric ultra sonic generator operating at 300 K.C. Each sample was agitated for ten minutes, then removed and allowed to cool. Difference spectra were obtained for these samples. The following day, difference spectra were obtained again for these same samples.

Plots of $\log I_o/I$ vs gms. of water per 100 gms. of sample were prepared for the three sets of spectra. The same procedure was followed as in the preparation of the grease curves.

CHAPTER III

RESULTS

Lubricating Greases

The averaged values of log I_o/I plotted against gms.
of water per 100 gms. of grease, or percent of water by
weight, produced curves which showed agreement with Beer's
Law. Figures (2) and (3) illustrate the linear nature of
the curves.

An anomalous step discontinuity occurred between .4 %
and .6 % water, with the curves either side of the step being
straight lines with their origins at 0% water. Unfortunately,
grease samples of the proper water content to fill in the
discontinuous region were not available. Evidence from the
oil and water curves tends to show that this step is not an
abrupt one.

The .68 mm cell was used for the purpose of investigating
the low water content portion of the curve, because of the
increased absorbtion of the thicker cell. The sensitivity
can thus be increased by using thicker cells, but it is
ultimately limited by the intensity of the infrared beam.
Increased cell thickness gives increased sensitivity, but
it also means a decreased range of observation. Therefore,
in an analysis of this type, sensitivity and the selection

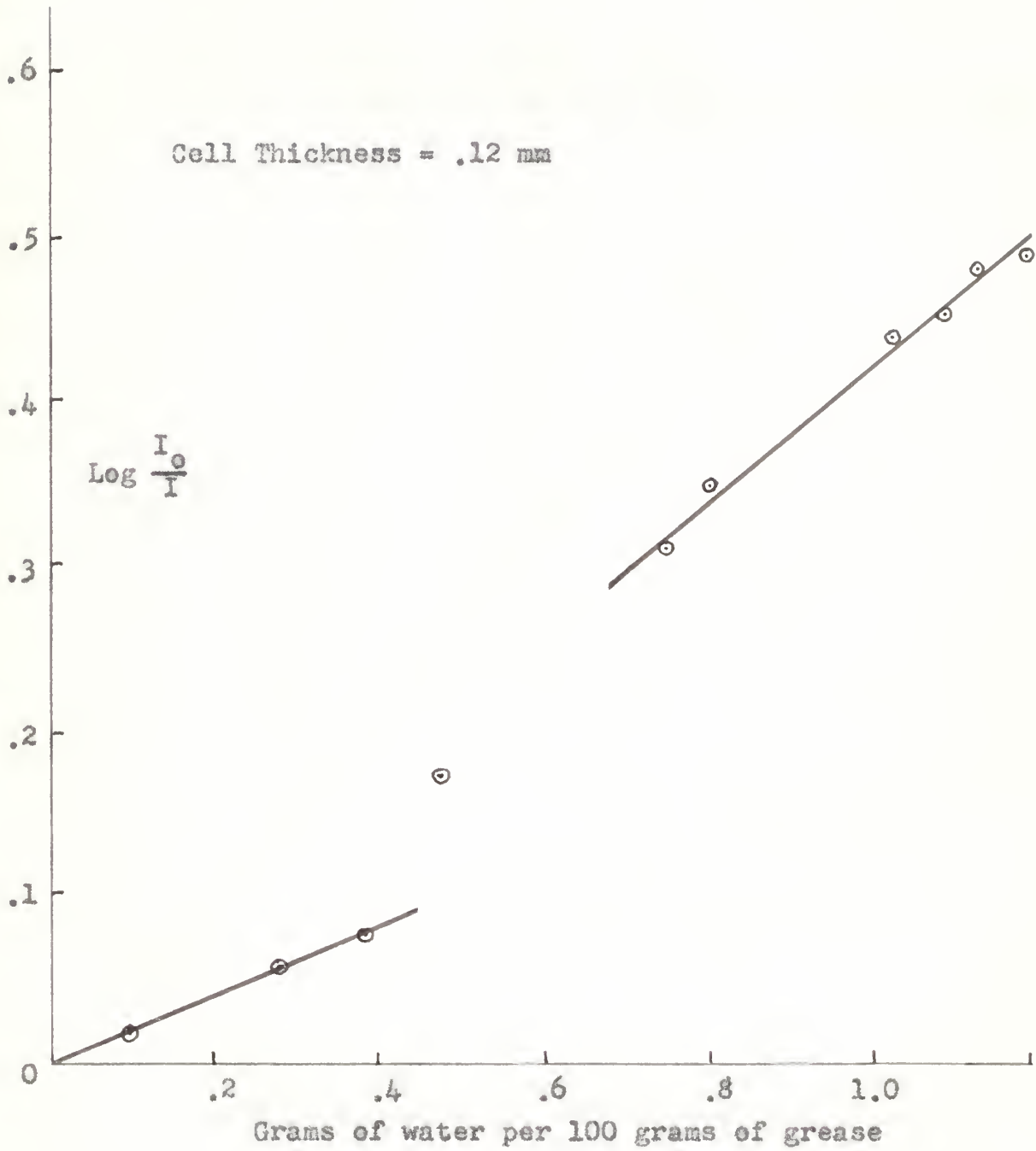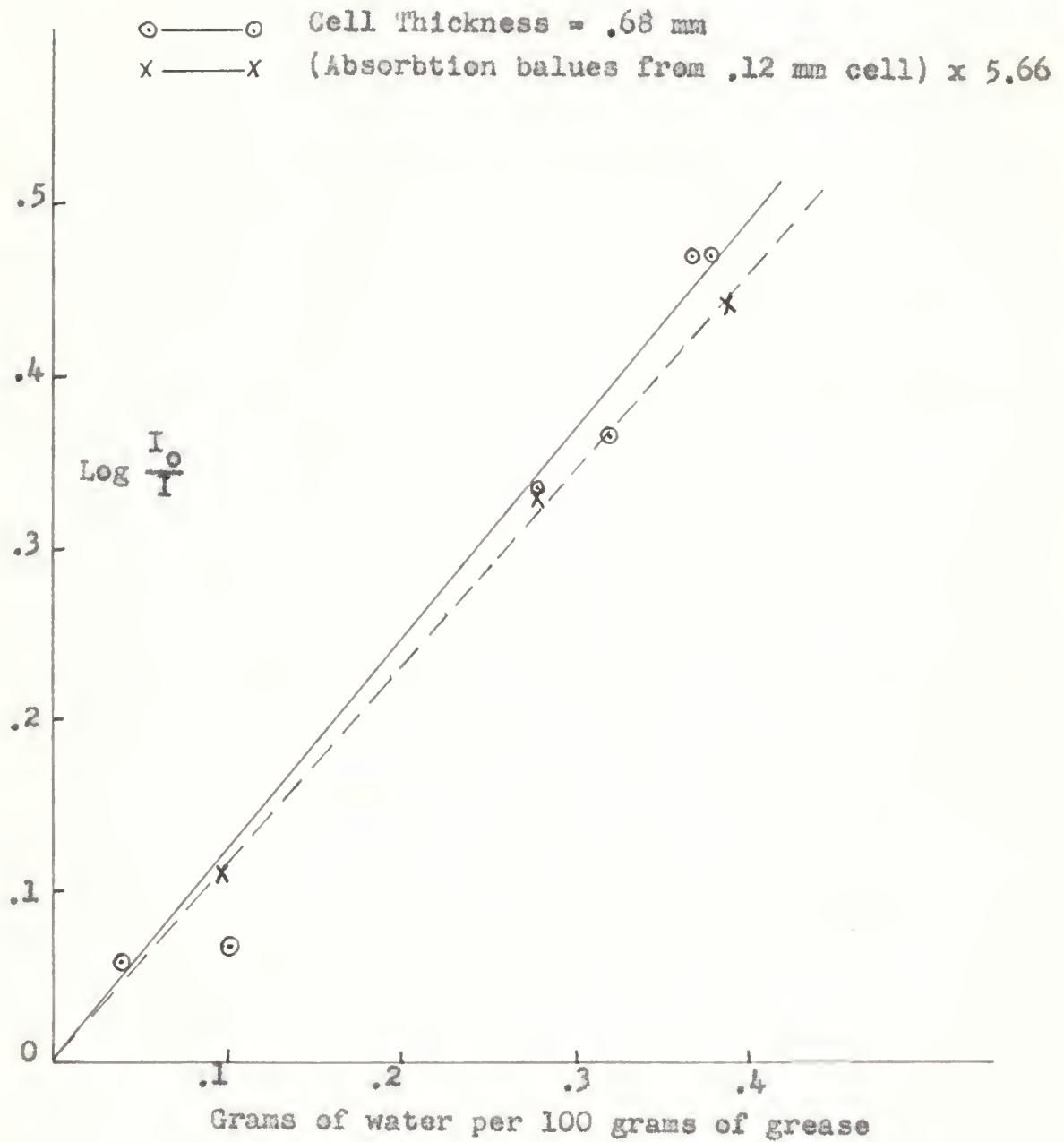FIGURE 2

Cell Thickness = .12 mm

$\text{Log } \dfrac{I_o}{I}$

Grams of water per 100 grams of grease

FIGURE 3

Cell Thickness = .68 mm

(Absorbtion balues from .12 mm cell) x 5.66

Log $\frac{I_o}{I}$

Grams of water per 100 grams of grease

of the cell thickness will depend upon the range of water concentrations it is desired to cover. In addition, it is much more difficult to prepare bubble free samples in the thicker cells.

The .68 mm cell covers a water concentration range from 0% to .47% water with excellent sensitivity. A very sizeable deflection, or peak, was recorded for a .04% water difference, while .47% water has an enormous peak. Because the .47% value is in the discontinuous region, its absorbtion is exceptionally high, and it is essentially the upper limit of the range of coverage for the .68 mm cell.

The Beer's Lambert Law can be stated as $\log I_o/I = -abc$; where $\log I_o/I$ is the absorbtion, a is the extinction coefficient, b is the cell length of the sample, and c is the sample concentration. From this, it can be seen that in comparing two samples having the same extinction coefficients and concentration, the ratio of absorbtion will depend only upon the ratio of cell thicknesses. In just such a manner the curves of Figures (2) and (3) were compared. The ratio of cell thicknesses is 68/12 which equals 5.66 . Absorbtion values from the .12 mm cell were multiplied by 5.66 and plotted alongside the curve of Figure (3). The dotted line through these points agrees with the solid line curve of Figure (3). This tended to confirm the Beer's Law agreement and also indicated that the larger number of small

bubbles in the .68 mm samples were not causing as much error as anticipated.

The accuracy of this experimental analysis depended mainly upon the accuracy of the Karl Fischer titration of the samples, and the non-reproducibility of cell thicknesses. Using Karl Fischer micro methods an accuracy in the region of ±.01% water by weight could be expected under excellent conditions. The grease samples containing .02% water were probably subject to a greater error. This titration error is incorporated in the results of this analysis since absorbtion is plotted against water concentration. The Perkin-Elmer Spectrophotometer will give a substantial difference spectrum when comparing two very thin films of polystyrene. Because of this sensitivity, the variation of the "handmade" cells introduced errors into the difference spectra of the greases.

In spite of the foregoing, a reasonable accuracy was achieved for values in the linear portions of the curves of Figures (2) and (3). Errors from the .12 mm cell recordings were normally less than .05 gms. of water per 100 gms. of sample grease. Errors from the .68 mm cell were usually less than .02 gms. of water per 100 gms. of sample.

Grease Components

The spectrum of the same mineral oil that was contained

in the grease coincided almost exactly with the spectra of the grease samples. This was not surprising since the grease is predominantly oil anyway. The agreement was so good at the 3 micron water band that several difference spectra were recorded, using a grease in the sample beam and the oil in the reference beam. The resulting values were completely in accord with the original grease data.

Several advantages accrue from the use of the anhydrous oil as a reference in the analysis scheme. Reference cells containing oil are more easily prepared than the grease cells, and the oil is a better reference than a grease because it is more homogeneous. A supply of the oil can be maintained in an anhydrous condition without great difficulty, whereas the grease is more apt to become contaminated by water from the air. Provided the oil can be kept dry, which doesn't appear to be any problem, the need for a Karl Fischer titration for standardizing the reference is eliminated. This is a distinct advantage to this analysis scheme because it removes the error introduced by the Karl Fischer titration.

The carboxyl group of the fatty acid displayed a sharp peak on the spectrum recording as was expected. Visual comparison with grease spectra indicated a negligible contribution by the fatty acid to the grease spectrum.

The lithium hydroxide monohydrate spectrum was also

examined, but yielded no pertinent information. A small
amount of excess caustic is normally present in lubricating
greases but, from the visual comparison of spectra, it
appears that it makes no significant contribution to the
grease spectrum.

Oil Samples

The results of the water in oil determinations were most
interesting. Figure 4A contains the plotted data of the oil
samples before agitation in the ultra sonic generator. It
is noteworthy that all the absorbtion values were much smaller
than the corresponding grease values, and that the curve
apparently levels off in the same region as the step discen-
tinuity in the grease.

Figure 4B shows the result of mixing in the ultra sonic
generator. The absorbtion values through .44% were unchanged,
but the remainder of the samples displayed an increase in
absorbtion. The resulting curve bears a striking similarity
to the grease curve of Figure 2.

Certain oil and water samples were checked again the
following day, with the results as indicated in Figure 4C.
The absorbtion values through .44% still remained constant,
but those values tested, which had shown an increased ab-
sorbtion after agitation, had decreased in absorbtion.

It is apparent that the finer dispersion created by the

FIGURE 4

(A) Before Agitation — Cell Thickness = .12 mm

(B) After Agitation

(C) After Standing One Day

- 24 -
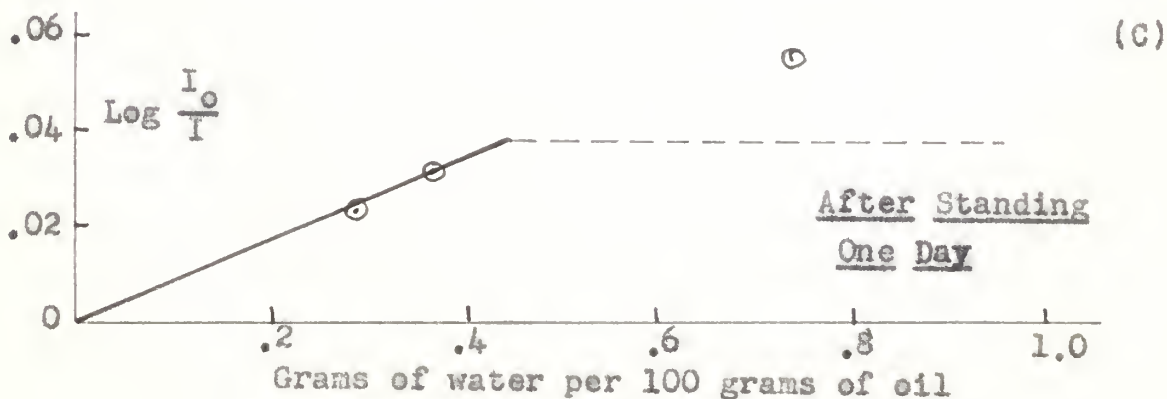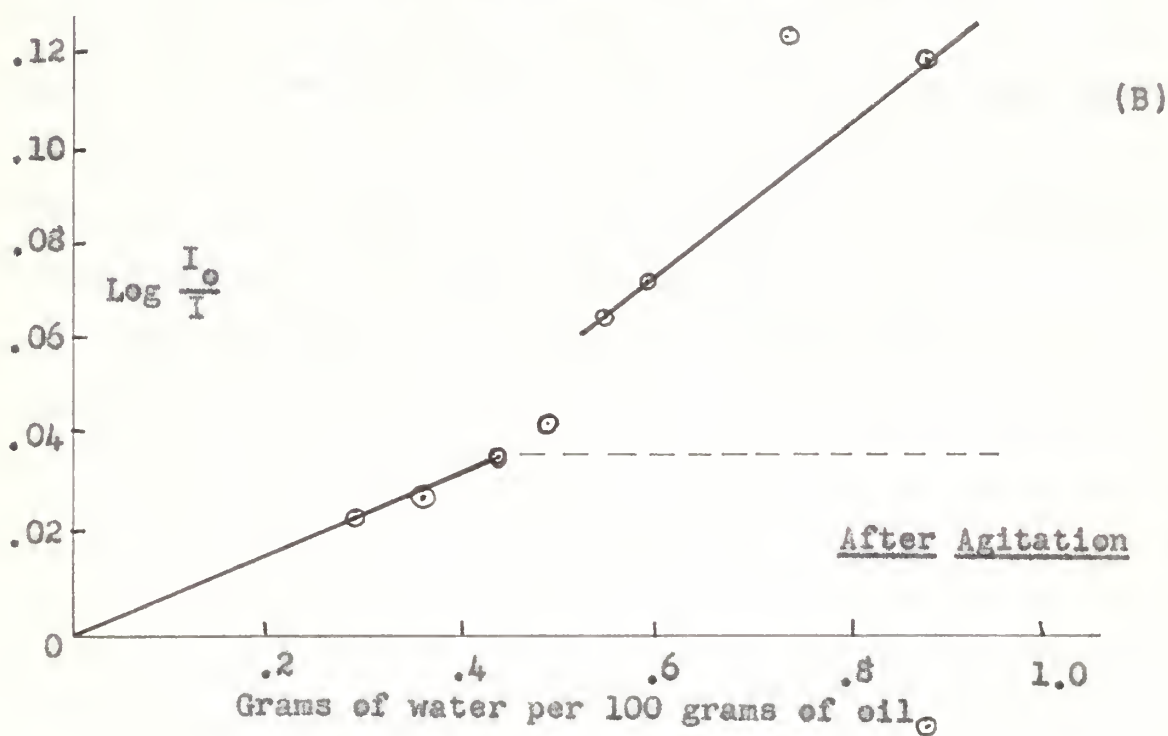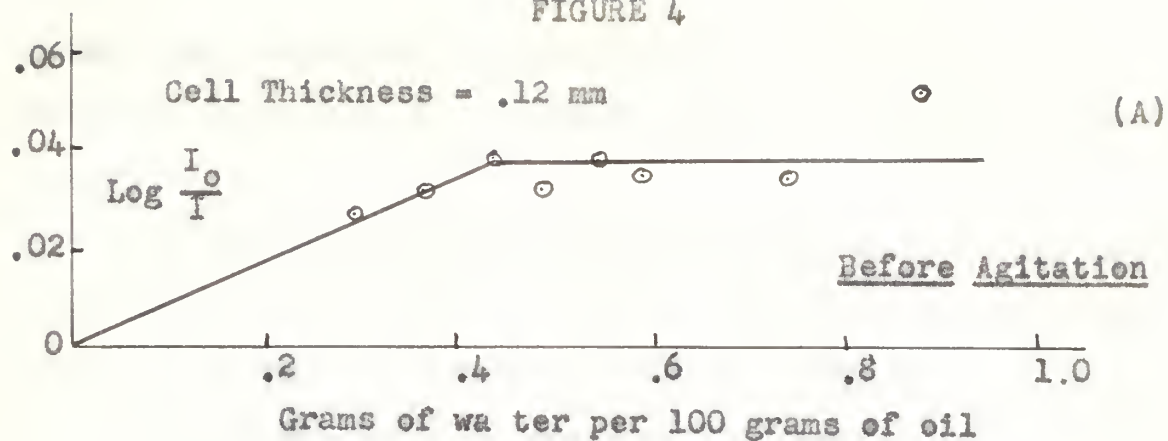
ultra sonic generator was not stable, and that the water below .44% was held in a manner stable to mechanical agitation.

The consistent absorbtion values for water in oil below .44% indicate that this method of analysis can be applied to the determination of water in oil, within obvious limits.

The maximum error observed in the portion of the curve below .44% was .04 gms. of water per 100 gms. of oil. The small absorbtion exhibited by these samples made measurement of the spectra more difficult and subject to increased error. The use of a thicker cell would increase the absorbtion and reduce the error involved in measuring I_o and I .

The relationships to the grease curves will be discussed in Chapter IV.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

Use of Infrared Absorbtion for Water Determination in Lubricating Greases

The results of this project indicate that analysis for small amounts of water in lubricating greases by infrared absorbtion methods is entirely feasible. Agreement with Beer's Law was displayed, and the errors involved are not prohibitive. While the accuracy of this scheme cannot compete with the Karl Fischer method at this time, it is certainly better than azeotropic distillation procedures. With the development of a satisfactory sample cell, it is believed that the accuracy should rival the Karl Fischer method, and may exceed it. For very small amounts of water, the sensitivity of the infrared analysis cannot be challenged by present methods of water determination.

The first problem to solve in perfecting this method, is that of the cell design. The "sandwich" method was sufficient for exploratory purposes, but is not considered adequate for an accurate quantitative analysis. It is suggested that a cell be constructed of permanent thickness, similar to a liquid cell, which can be filled with grease by a powerful syringe or grease gun. Special fittings may or may not be necessary to accomplish this. The cell windows

should be of quartz, which gives excellent transmission up to 5 microns, and is vastly stronger, harder, and more water resistant than sodium chloride crystals. The cell thicknesses can be measured accurately by interference fringes. Reference (31) describes a method of cell thickness measurement. In filling the cell, care must be taken to insure the portion of the grease in the beam path is free of any large bubbles.

When the cell thickness problem is alleviated, attention can be directed to empirical corrections for finite slit width and optical attenuation, if they appear to be necessary.

Before venturing further, many more samples of Li grease should be tested, and the discontinuous region filled in. Since most commercial Li greases contain less than .5% water by weight, the discontinuity may not cause serious difficulty in analyzing this type of grease for water. Greases of other types, such as Na and Ca greases, should be investigated thoroughly and compared with the results of this Li grease. It is suggested that the corresponding mineral oils be checked at the same time for their use as references.

This method can be applied in the plane for control purposes as well as in the laboratory for investigative work. Infrared analysis could be a valuable analytical tool in the control of dehydration during the manufacture of

grease. A scheme such as the following could be applied.

Maintain the infrared spectrophotometer in a constant humidity room and in good adjustment. Have at least four cells of the type just described, with their cell thicknesses accurately measured. Maintain anhydrous samples of the mineral oils used in the greases being manufactured. When a grease is to be analyzed for water, fill three or four cells with the grease and fill the reference cell with the particular mineral oil in use. Make the recordings following the procedure described in Chapter II and average the results. A plot of percent transmission vs. concentration, called a "working curve", could be used to good advantage here, and saves computing the $\log I_o/I$ values. However, the straight line Beer's Law curve can probably be read more accurately. Standard analytical procedures should be employed in averaging the results, and in disregarding values of questionable validity.

Discussion of Results

The res ults of this project not only tend to show the value of infrared absorbtion as an analytical device, but also as a means of investigating the manner in which water is held in greases. Interpretation of the grease and water in oil curves may yield some valuable information regarding this matter.

A useful analogy to employ when examining infrared difference spectra is that of fog and rain. The small water particles of fog are very difficult to see through, while the larger raindrops do not restrict the vision as much. The same considerations apply to the infrared beam and the water particles in the sample.

At a given concentration of water, the smaller water particles will produce a higher infrared absorbtion and greater reflection of the infrared beam. The magnitude of the reflection is not known and it should be investigated. It is likely that reflection increases with the concentration of small particles.

In discussing the oil curves, it was pointed out that the absorbtion values were much lower than were the absorbtions for the corresponding water concentrations in the greases. Since both were obtained from difference spectra, it can be construed that the water particles in the oil were larger than those in the grease samples. This is more or less to be expected anyway. Considering Figure 4, it is seen that the curve increases to somewhere around .44% and then levels off, and that this section of the curve is not affected by mechanical agitation. Apparently, the oil can hold water in a stable manner up to about .44%. Above this "saturation point", the water is held in some loose manner,

in very large particle size, because the absorbtion curve levels off. These large particles can be easily broken up and dispersed by mechanical agitation. The high absorbtion values of Figure 4B indicate that smaller particles are not stably dispersed however, and tend to coalesce, as shown in Figure 4C. The water below .44% seems to be held in some stable manner and in a fairly large particle size, for in the greases, the corresponding absorbtions are much higher. These water particles, then, are stable to mechanical agitation, but can be reduced in size by heating and by the polar soap particles during grease manufacture.

It may be inferred that the step discontinuity of the grease curve is tied up with the mineral oil in some way. Pure paraffin oil, and other saturated alkanes, have water in oil solubilities 10 to 100 times smaller than the .44% value.[33, 34] If the mineral oil tested was pure, then the solubility factor can be considered present but unimportant. The water must be held in some other stable manner then. While not specifically applicable, reference (14) presents an interesting concept about stable water particles dispersed in oil. Very briefly, it consists of the oil particles squeezing charged polar water particles into irregular shapes covered by rigid neutral films. This forms a stable dispersion of "water sacks" in oil. However, other polar substances must be present. This concept is

not mentioned as an explanation of the observed facts in this
case, but on the basis that it might provide for further
thought and investigation.

It may be concluded, then, that the mineral oil can hold
dispersed water particles of fairly large size in a stable
dispersion. The limit of this capacity is in the neighborhood
of .44 gms. of water per 100 gms. of oil, and solubility is
not an important factor unless other polar substances are
present.

In greases, the strong polar soap fibers can easily
associate with water particles in a stable fashion. This
effect, plus heating during manufacture and the presence of
other polar substances in greases, tends to produce a stable
dispersion of fine water particles. This is evidenced by
the high infrared absorbtion of water in grease compared to
water in oil. Below the region of .44%, these effects reduce
the size of the stable water particles in oil. Above the
discontinuous region the same effects are strong enough to
hold the dispersed water particles, which the oil will not
accept, in a stable fashion and in a smaller particle size
than below the discontinuity. This is indicated by the higher
absorbtion and greater slope of the grease curve above the
discontinuity. It may be concluded then, that below .44% in
these Li greases, both the oil and the soap contribute to
the manner in which the water is held; while above the

discontinuity, the soap determines the manner in which the water is held. Other polar substances in greases are included with soap in the foregoing statement. Some mechanism of hydration or coordination is likely in the latter case, along with physical trapping of the water particles by the soap fibers.

It is interesting to note that most Li greases contain less than .5% water. Is this merely a coincidence, or does the step discontinuity have some relation to the structure and properties of this grease?

Further investigation should naturally include evaluation of other types of greases. Varying the amounts and types of soaps and oils should provide interesting information since it is to be expected that the soap fiber size and configuration should affect the water picture. The effects of each of the numerous grease additives should be determined also. Since the breakdown of greases is associated with fiber disintegration, a change in the water picture would be expected after mechanical working. Preparation of curves similar to Figure 2 before and after mechanical working of a grease is recommended.

It can be gathered from the foregoing discussion that the manner in which water appears in grease is not a simple one. Because of the relationships between the different

grease components, it will be very difficult or impossible to evaluate the various effects relating to water and to add them up quantitatively. The Law of Additivity of Optical Densities[28] could be applied in such a scheme, but only limited success can be expected. Nevertheless, in continuing the study of the problem of water in greases, careful consideration should be given to the many ways in which the infrared spectrophotometer can be put to use.

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VITA

James Edward Edmundson was born April 17, 1927 in Long Beach, California, the son of Lucile Ehle and Edward Harold Edmundson. Upon graduation from Central High School, Washington, D. C., in June 1944, he entered the Navy V-12 program and attended Villanova University and Muhlenberg College, for one semester each. He left the V-12 program to attend the Naval Academy Preparatory School at Camp Peary, Virginia. He received a Presidential Appointment to the United States Naval Academy and entered in June 1945. In June 1949 he graduated with honors and received a degree of Bachelor of Science.

Lt. Edmundson has served aboard the destroyer CONE and minesweepers SISKIN and PILOT. From August 1953 to August 1955 he attended the United States Naval Postgraduate School and graduated with a degree of Bachelor of Science.

Mr. Edmundson was married in June 1952 to the former Jean Gray of Watertown, Massachusetts. They have one child, Jeffrey Scott.